

PATENT SPECIFICATION

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Complete Specification Accepted: Sept. 3, 1934.

PROVISIONAL SPECIFICATION.

Improvements in or relating to the Manufacture of Cyanhydrins.

We, THE TRIPLEX SAFETY GLASS COMPANY LIMITED, a British Company, of 1, Albemarle Street, Piccadilly, London, W.1, LESLIE VIVIAN DONALD SCORAH, a British Subject, and JOHN WILSON, a British Subject, both of Triplex Works, Eccleshall Road, King's Norton, Birmingham, do hereby declare the nature of this invention to be as follows:—

This invention consists of improvements in or relating to the manufacture of polymerisable organic compounds and has particular reference to the economical production of unsaturated nitriles (such as methacrylonitrile).

Suggestions have hitherto been put forward for the production of unsaturated nitriles of acrylic acid and its homologues, but these have been unsatisfactory from a commercial point of view mainly because the reactions leading to the formation of the unsaturated nitrile are so apt to get out of control. For example, if acetone is treated with hydrocyanic acid to produce acetone cyanhydrin, the reaction is highly exothermic and is apt to take place irregularly and with extreme violence whereby dangerous accidents may occur.

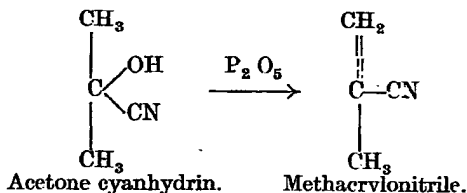
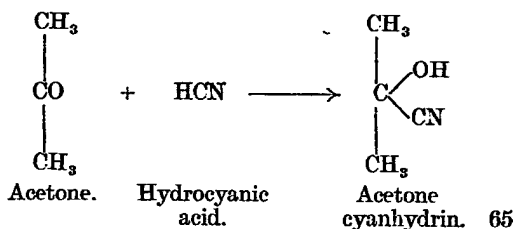
We have, however, discovered that it is possible under certain conditions to obtain acetone cyanhydrin by reaction of hydrocyanic acid with acetone by an approximately quantitative reaction which is under complete control.

Further the production of an unsaturated nitrile such as methacrylonitrile from the corresponding cyanhydrin by dehydration has hitherto proved commercially impracticable, but we have found that there again the reaction may be made practical and commercial if carried out under certain conditions.

According to this invention a process for the manufacture of unsaturated nitriles of homologues of acrylic acid (such for example as methacrylonitrile) includes as a first step the heating of an aliphatic ketone, such as acetone, to boiling point in the presence of a basic catalytic agent, preferably an organic basic reagent (such for example as piperidine)

and the addition of a molecular quantity of liquid hydrocyanic acid at such a rate that the ketone remains steadily boiling. 55

This invention also includes the further step of dehydrating the cyanhydrin, such as acetone cyanhydrin, with a powerful dehydrating agent such as phosphorus pentoxide in the presence of a basic organic catalytic agent, such as quinoline. 60 The reactions in the case of acetone are represented by the following equations:—



The following is an example of one method of carrying this invention into effect:— 70

600 parts by volume of acetone are run into a container and 30 parts by volume of piperidine are added.

The mixture is gently heated up to the boiling point of acetone and is kept simmering in a vessel fitted with efficient condensing means. 75

300 parts by volume of liquid hydrocyanic acid are then run in slowly, at such a rate that the acetone remains steadily boiling. 80

After the whole of the hydrocyanic acid has been added, the liquid is kept at the boil for a further period of about an hour in order to ensure that equilibrium has been established. 85

The boiling of the liquid effects agita-

tion, but if desired mechanical agitation may also be used.

To the cooled mixture is then added 50% more concentrated sulphuric acid than is necessary to neutralise the piperidine employed and the liquid is transferred to a vacuum distillation apparatus and is distilled at 50° to 60° C. on a water bath maintained at 80° to 90° C. until most of the hydrocyanic acid and acetone have come over. The pressure is then reduced to 15 to 20 mm. of mercury when the acetone and the hydrocyanic acid which have not reacted together with any water present distil off. The temperature of the vapour distilling over is first approximately 75° C. and then falls gradually to about 67° C. At this temperature the pure acetone cyanhydrin distils over and is collected separately.

To 360 parts by weight of the acetone cyanhydrin and 100 parts by weight of technical quinoline are added slowly with cooling and vigorous shaking 600 parts by weight of phosphorus pentoxide. When the addition is complete the temperature is gradually raised to approximately 100° C.

Slow but efficient stirring must be continued while the temperature continues to rise and the methacrylonitrile distils over together with small amounts of decomposition products such as hydrocyanic acid and acetone. The temperature of the bath ultimately reaches 250° C. and by that time most of the nitrile has distilled over. The residue of nitrile remaining in the mix may be removed by steam distillation or by the addition of water to the hot reaction mixture.

The distillate of methacrylonitrile is purified by washing twice with 2 N. caustic soda, once with N. sulphuric acid and again with 2 N. caustic soda after which the liquid is distilled through a suitable fractionating column. If desired, the methacrylonitrile may be distilled over a drying agent to remove water, or the first portion of the distillate containing most of the water may be collected separately and the water therein removed by any suitable mechanical means. Alternatively, the fraction containing the water may be redistilled with a subsequent batch of product.

The pure methacrylonitrile distils over at 88–90° C. under atmospheric pressure.

If desired the reaction may be facilitated and caking of the mixture containing phosphorus pentoxide reduced by the addition of a diluent, e.g. 100 parts by weight of tetrahydronaphthalene.

The nitrile of methacrylic acid as produced in accordance with this invention is particularly useful as a polymerisable substance for the manufacture of tough transparent articles, films, filaments, adhesives, lacquers, moulding powders and thermoplastic materials.

Again the polymerisation products may be employed in the manufacture of safety glass either in the formation of the strengthening layer or as a uniting agent, cement, or enamel.

Dated this 1st day of March, 1933.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London,
E.C.1,
Chartered Patent Agents.

COMPLETE SPECIFICATION.

Improvements in or relating to the Manufacture of Cyanhydrins.

We, THE TRIPLEX SAFETY GLASS COMPANY LIMITED, a British Company, of 1, Albemarle Street, Piccadilly, London, W.1, LESLIE VIVIAN DONALD SCORAH, a British Subject, and JOHN WILSON, a British Subject, both of Triplex Works, Eccleshall Road, King's Norton, Birmingham, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention consists in improvements in or relating to the manufacture of cyanhydrins of the aliphatic series.

Suggestions have hitherto been put forward for the production of unsaturated

nitriles of acrylic acid and its homologues but these have been unsatisfactory from a commercial point of view mainly because the reactions leading to the formation of the unsaturated nitrile are so apt to get out of control. For example, if acetone is treated with hydrocyanic acid to produce acetone cyanhydrin, the reaction which is highly exothermic is apt to be delayed and to take place irregularly and with extreme violence whereby dangerous accidents may occur.

We have, however, discovered that it is possible under certain conditions to obtain e.g. acetone cyanhydrin by the treatment of hydrocyanic acid with acetone by a reaction which goes to equilibrium

and which is under complete control.

According to this invention there is provided a process for the manufacture of a cyanhydrin of the aliphatic series, for example acetonecyanhydrin, which comprises adding to an aliphatic ketone, for example, acetone, maintained at boiling point and containing a base dissolved therein, a molecular quantity of hydrocyanic acid.

The hydrocyanic acid employed is preferably in the liquid state but if desired it may be added in the form of gas.

Among the bases that may be employed in the present process may be mentioned alcoholic caustic soda, aqueous caustic soda, gaseous ammonia, aqueous ammonia, pyridine, piperidine, quinoline, primary, secondary or tertiary amines, potassium cyanide and sodium cyanide.

After the addition of the hydrocyanic acid the mixture may be maintained at boiling point for such a period as to ensure that equilibrium conditions have been attained. The time necessary to reach the equilibrium varies with the nature and amount of the base used. In the case of a strong base such as caustic soda or piperidine, equilibrium is reached almost immediately. In the case of a weaker base such as pyridine and using quantities such as those specified in the examples which follow, it is necessary to boil for half-an-hour after the whole of the reactant has been added. In practice, an organic base such as pyridine is preferred since with this base the tendency to side reactions is minimised. Side reactions also take place if larger quantities of weak base are used or if the boiling is continued beyond the time necessary to reach equilibrium.

Recovery of cyanhydrin from the reaction mixture is brought about by acidifying the mixture and distilling under reduced pressure. The acid employed for acidifying is preferably a relatively non-volatile mineral acid such as sulphuric acid and this may be added in such amount that there is present 50% more acid than is necessary to neutralise the basic compound employed in the reaction.

Cyanhydrins prepared in accordance with this invention may be employed for example in the preparation of unsaturated nitriles of homologues of acrylic acid, the cyanhydrin being dehydrated with a powerful dehydrating agent such as phosphorus pentoxide in the presence of a soluble base.

In the dehydrating step of the process, the base and the dehydrating agent may conveniently be added to the cyanhydrin

with cooling and with efficient agitation.

The addition of the base and powerful dehydrating agent (e.g. phosphorus pentoxide) to the cyanhydrin may be carried out either by adding the correct amount of base followed by the phosphorus pentoxide (in which case it is necessary to cool efficiently during the addition of the phosphorus pentoxide, otherwise the heat developed is so great that the reaction takes place prematurely) or by adding the whole of the phosphorus pentoxide to the cyanhydrin followed by the requisite amount of the base. In the latter case little or no heat is evolved during the addition of the phosphorus pentoxide and it is not therefore necessary to cool. Heat evolution, however, takes place as soon as the base is added. The unsaturated nitrile may be recovered from the reaction mixture by distillation and any nitrile still remaining in the mixture after distillation may be recovered by the addition of water or by steam distillation.

In one preferred form of the process for the conversion of the cyanhydrin to the corresponding unsaturated nitrile, a non-reactive diluent is mixed with the cyanhydrin before or after the addition of the dehydrating agent. The diluent may comprise an organic liquid, e.g. tetrahydronaphthalene.

The following are examples of two methods of carrying this invention into effect.

EXAMPLE I.

30 parts by volume of piperidine are added to 600 parts by volume of acetone.

The mixture is placed in a vessel provided with efficient condensing means and is gently heated to the boiling point of the mixture.

300 parts by volume of liquid hydrocyanic acid are then run in slowly, at such a rate that the mixture remains steadily boiling.

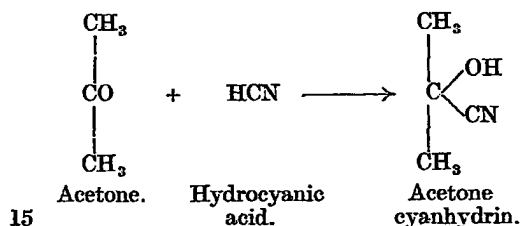
After the whole of the hydrocyanic acid has been added, the liquid is kept at the boil for a further period of about an hour in order to ensure that equilibrium has been established.

The boiling of the liquid effects agitation, but if desired mechanical agitation may also be used.

To the cooled mixture is then added 50% more concentrated sulphuric acid than is necessary to neutralise the piperidine employed and the liquid is transferred to a vacuum distillation apparatus and is distilled at 50° to 60° C. on a water bath maintained at 80° to 90° C. until most of the hydrocyanic acid and acetone have come over. The pressure

is then reduced to 15 to 20 mm. of mercury when the remaining acetone and hydrocyanic acid distil over together with any water present. The temperature of the vapour distilling over is first approximately 75° C. and then falls gradually to about 67° C. At this temperature the pure acetone cyanhydrin distils over and is collected separately. (Refractive index at 22.5° C. 1.3970).

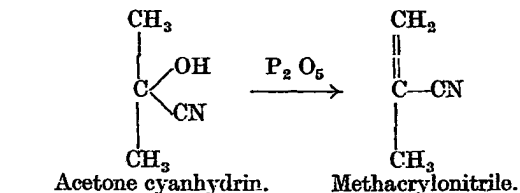
The reaction may be represented by the following equation:—



Cyanhydrin prepared in accordance with this invention may be employed for example in the preparation of unsaturated nitriles of homologues of acrylic acid. Thus, to prepare methacrylonitrile, to 360 parts by weight of the acetone cyanhydrin and 100 parts by weight of technical quinoline are added slowly with cooling and vigorous shaking 600 parts by weight of phosphorus pentoxide. When the addition is complete the temperature is gradually raised to approximately 100° C.

Slow but efficient stirring must be continued while the temperature continues to rise and the methacrylonitrile distils over together with small amounts of decomposition products such as hydrocyanic acid and acetone. The temperature of the bath ultimately reaches 250° C. and by that time most of the nitrile has distilled over. The residue of nitrile remaining in the mix may be removed by steam distillation or by the addition of water to the hot reaction mixture.

The reaction may be represented as follows:



The distillate of methacrylonitrile may be fractionally distilled. Alternatively it may be washed with a saturated solu-

tion of sodium metabisulphite until free from acetone, washed with a solution of 2 N. caustic soda and finally distilled through a fractionating column. If desired, the methacrylonitrile may be distilled over a drying agent to remove water, or the first portion of the distillate containing most of the water may be collected separately and the water therein removed by any suitable mechanical means. Alternatively, the fraction containing the water may be redistilled with a subsequent batch of product.

The pure methacrylonitrile distils over at 89–90° C. under atmospheric pressure.

If desired the reaction may be facilitated and caking of the mixture containing phosphorus pentoxide reduced by the addition of a diluent, e.g. 100 parts by weight of tetrahydronaphthalene.

EXAMPLE II.

493 parts by weight of acetone (as per British Standard Specification No. 509–1933) and 20 parts by weight of pyridine (the commercially available pyridine fraction of a coal tar distillate is suitable) are placed in a large shallow vessel provided with a stirrer, an efficient reflux condenser, and means, e.g. a water bath for raising the temperature to any desired degree and maintaining it.

The mixture of acetone and pyridine is heated to boiling point and kept at a gentle simmer while 230 parts by weight of hydrocyanic acid are run in in such a manner that the rate of boiling is steadily maintained. After all the hydrocyanic acid has been added, the contents are kept at boiling point for a further half hour until equilibrium is reached.

The equilibrium mixture is then cooled by running cold water through the jacket. 77 parts by weight of dry pyridine are then added after which 750 parts by weight of granular phosphorus pentoxide are also added while stirring and cooling. An oil bath is now substituted for the water bath and the temperature is slowly raised to about 90° C. The dehydration reaction commences, the contents begin to froth and the temperature rapidly rises. During this stage a further 77 parts by weight of pyridine are added. Methacrylonitrile, acetone and hydrocyanic acid distil over. The product is fractionated with approximately the following yields. 55% of the theoretical quantity of nitrile is obtained, 25% of the original acetone and hydrocyanic acid are recovered as such and approximately 20% of the original materials are lost in various side reactions including the polymerisation of hydro-

and hydrolysis of the cyanhydrin.

Alternatively, the equilibrium mixture after cooling by running cold water through the jacket has added to it with stirring 750 parts by weight of granular phosphorus pentoxide. An oil bath is then substituted for the water bath and 77 parts by weight of dry pyridine are added. The temperature rises and is assisted by heating the oil bath. When the temperature reaches approximately 90° C. the dehydration reaction commences. The subsequent steps in the process are carried out as described above.

The nitrile of methacrylic acid as produced in accordance with this invention is particularly useful as a polymerisable substance for the manufacture of tough transparent articles, films, filaments, adhesives, lacquers, moulding powders and thermoplastic materials.

Again the polymerisation products may be employed in the manufacture of safety glass either in the formation of the strengthening layer or as a uniting agent, cement or enamel.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the manufacture of a cyanhydrin of the aliphatic series, for example acetonecyanhydrin, which comprises adding to an aliphatic ketone, for

example, acetone, maintained at boiling point and containing a base dissolved therein, a molecular quantity of hydrocyanic acid.

2. A process as claimed in Claim 1 wherein the hydrocyanic acid is in the liquid form.

3. A process as claimed in claim 1 or claim 2, wherein the base comprises an organic compound of heterocyclic series e.g., pyridine, piperidine or quinoline.

4. A process as claimed in any one of the preceding claims wherein after the addition of the hydrocyanic acid the mixture is maintained at boiling point for such a period as to ensure that equilibrium conditions have been attained.

5. A process as claimed in any one of the preceding claims wherein the cyanhydrin is recovered from the reaction mixture by acidifying the said mixture with mineral acid, preferably relatively non-volatile mineral acid, e.g. sulphuric acid, and distilling under reduced pressure

6. A process for the manufacture of a cyanhydrin substantially as described in either of the specific examples hereinbefore set forth.

7. Cyanhydrins whenever prepared by the processes claimed in any one of the preceding claims.

Dated this 22nd day of February, 1934

BOULT, WADE & TENNANT,
111/112, Hatton Garden, London, E.C.1,
Chartered Patent Agents.